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Electrodeposition of Biaxial Textured Films

Contractual Origin of Invention

The United States Government has rights in this invention under Contract No. DE-AC36-99GO10337 between the United States Department of Energy and the National Renewable Energy Laboratory, a Division of the Midwest Research Institute.

Technical Field

This invention relates to substrates having biaxially textured buffer layers, and more specifically, to superconducting devices incorporating flexible substrates having biaxially textured buffer layers.

Background Art

Superconducting materials, which are characterized by their very desirable ability to conduct electricity without resistance, can be deposited onto a variety of substrates for use in a variety of applications, including conductive wires, tapes, and many electronic devices. To be commercially viable, superconducting materials used in these applications must have a high critical current density---the maximum current density a superconductor can carry at a given temperature and magnetic field, because high electrical current is required to power any significant load. It has been shown that superconducting materials formed with biaxially textured crystalline structures have superior critical current densities. Generally, texturing refers to a cluster structure comprising a number of crystal particles that have the same crystal orientation (longitudinal axial direction) in a polycrystalline or other material. Biaxial texturing for superconducting materials is a term that is well-understood by persons skilled in the art. However, for a general concept, uni-axial texturing describes a polycrystalline material in which a significant number of crystal particles in the cluster structures are oriented uniformly in one of the three axial directions in three-dimensional space, while there is little or no uniformity of crystal orientation in the other two axial directions. In contrast, biaxial texturing describes material in which a significant number of the crystal particles in the cluster structures are oriented generally

uniformly in all of the three axes. Generally, such biaxially textured superconductor materials appear under a microscope to comprise numerous, elongated, crystalline structures oriented in a common longitudinal direction.

The most common way to accomplish biaxial texturing in a superconducting material is to deposit the superconductor precusor materials onto a substrate, which itself has biaxial texture. Then, during the deposition and the resulting growth of the superconductor material, the growing crystalline particles tend to conform themselves to the same biaxially textured, crystalline orientation of the substrate. Therefore, by growing the superconductor material on a biaxially textured substrate, the biaxial texturing of the substrate develops and is maintained in the superconductor material.

One drawback to depositing a superconducting material directly onto a substrate, particularly a metal substrate, is that many materials used to form superconductors interact adversely with the substrate in a manner that degrades the superconductor material, especially during the high temperatures at which the superconductor materials are deposited or processed. To overcome this adverse interaction, a buffer layer of material is often deposited between the substrate and the superconducting material to form a chemical barrier between the metal substrate and the superconductor. Examples of suitable buffer layers are reported in U.S. Patent Nos. 6,296,701 to Christen et al., 6,261,704 to Paranthaman et al., and 6,156,376 to Paranthaman et al.

Gold is an attractive candidate for a buffer layer material for superconductor structures because a relatively thin film of gold provides a substantially inert barrier between the metal substrate and the superconductor, and it can be applied relatively inexpensively by electrodeposition. However, conventional electrodeposition of gold, which is performed at a high current density (1-5 A/cm^2) for a short period of time (1-10 minutes), does not result in the biaxial texturing needed for optimal superconductor performance.

Disclosure of the Invention

Accordingly, a general object of the present invention is to provide a method of depositing gold onto a substrate in a manner that forms a gold buffer layer with biaxial texturing for electrical and electronic applications.

A more specific object of this invention is to provide a method of electrodepositing gold having biaxial texturing onto a substrate by electrodeposition.

Another object of the invention is to provide a method of forming an electronically active device with a gold buffer layer that has biaxial texturing on a metal substrate, upon which a superconducting material with biaxial texturing can be deposited and grown.

Additional objects, advantages, and novel features of this invention are set forth in the description and examples below, and others will become apparent to persons skilled in the art upon examination of the following specification or may be learned by practicing the invention. The objects and advantages of the invention may be realized and attained by the instrumentalities, combinations, compositions, or methods particularly included in the appended statements.

To achieve the foregoing and other objects and in accordance with the purposes of the present invention, as embodied and described herein, a method of forming a gold buffer layer having biaxial texturing on a substrate includes electrodepositing gold onto a surface of the substrate at a current density of less than about 5.0 mA/cm^2, preferably in a range between about 0.10 and 3.5mA/cm^2, for at least about one minute, preferably in a range between about one and 60 minutes. The gold layer may be subsequently annealed for between 12 and 60 hours at between 500 and 600 °C to increase the biaxial texturing.

A biaxially textured gold buffer layer can be used to make a superconductive article, according to this invention by electrodepositing it onto a surface of a substrate as a buffer layer and then depositing and growing a biaxially textured, superconducting material on the biaxially textured gold buffer layer by one or more conventional deposition methods, such as by pulsed-laser deposition. If desired, the gold layer can be annealed for between 12 and 60 hours at between 500 and 600 °C to increase its biaxial texturing. The substrate can be any suitable material that can maintain its integrity in these temperatures,

such as metal. It is preferred that the substrate also be biaxially textured in order to enhance biaxial texturing in the gold buffer layer and ultimately in the superconductor material itself. Suitable substrates can comprise nickel, tungsten, chromium, titanium, palladium, copper, and alloys thereof. The superconducting material may comprise any of a variety of known high temperature, superconductor materials, such as, but not limited to, YBCO, BSCCO, TBCCO, PBSCCO, TSBCCO, TPSBCO, HBCCO, or HBCO.

<u>Brief Description of the Drawings</u>

The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the preferred embodiments of the present invention, and together with the descriptions serve to explain the principles of the invention.

In the Drawings:

Figure 1 is an isometric, diagrammatic view of a biaxially textured superconductor article with a biaxially textured gold buffer layer between the substrate and the superconducting layer according to this invention;

Figure 2 is a theta-2-theta scan of gold electrodeposited onto a nickel substrate by conventional electrodeposition;

Figure 3 is a theta-2-theta scan of gold electrodeposited onto a nickel substrate according to an embodiment of the present invention;

Figure 4 is a theta-2-theta scan of gold electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 5 is a theta-2-theta scan of gold electrodeposited onto a nickel substrate according to an embodiment of the present invention;

Figure 6 is a pole figure scan of gold, which was electrodeposited onto a nickel substrate according to an embodiment of the present invention;

Figure 7 is a theta-2-theta scan of gold, which was electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 8 is a pole figure scan of gold, which was electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 9 is an omega scan of gold, which was electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 10 is a phi scan of gold, which was electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 11 is a theta-2-theta scan of gold, which was electrodeposited onto a nickel substrate according to an embodiment of the present invention;

Figure 12 is a theta-2-theta scan of a gold, which was electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 13 is a pole figure scan of gold measured, which was electrodeposited onto a nickel substrate and then annealed according to an embodiment of the present invention;

Figure 14 is a theta-2-theta scan of gold, which was electrodeposited onto a nickel substrate according to an embodiment of the present invention; and

Figure 15 is a theta-2-theta scan of YBCO deposited onto a gold buffered nickel substrate according to an embodiment of the present invention.

Best Modes for Carrying Out the Invention

An example section of a superconducting article 10 with a biaxially textured superconductor layer 12 grown epitaxially on a biaxially textured, gold buffer layer 14, according to this invention, on a substrate 16 is shown diagrammatically in Figure 1. A significant feature of this invention, as illustrated in Figure 1, is that it provides a method of electrodepositing a gold buffer layer 12 having biaxial texturing onto a substrate 14, so that a biaxially textured superconductor material 12 or other electrically active layer can be grown on the gold buffer layer 14. The gold buffer layer 14 is biaxially textured according to this invention, because such biaxial texturing in the gold buffer layer 14, as indicated diagrammatically by arrows 32 in Figure 1, will induce corresponding biaxial texturing in the superconductor layer 12, as indicated diagrammatically by arrows 34, 36 in Figure 1.

Therefore, a significant part of this invention includes attaining biaxial texturing in the gold layer 14, as will be described in more detail below.

The substrate 16 used in the present invention may be either a flexible or rigid metal or other material that can be fabricated into a variety of shapes, sizes and thicknesses. For conductive wire and tape applications, for example, the metal substrate 16 may be fabricated over long lengths and/or areas. The substrate 16 may have any desired thickness. For flexible metal substrates, for example, a thickness between about 0.005 mm and 0.05 mm is particularly useful for this invention. Suitable metals include nickel, copper, titanium, palladium, and/or combinations or alloys thereof, including nickel:tungsten and nickel:chromium alloys. The substrate 16 may also be biaxially textured, as indicated by arrows 30 in Figure 1. Biaxially texturing the metal substrate 16 can be done, for example, by a suitable industrially scalable rolling process known in the art, such as the rolling assisted biaxially textured substrates (RABiTS) process. While a biaxially textured substrate 16 is not absolutely necessary to practice this invention, use of a biaxially textured substrate 16 is helpful, in fact, very much preferred, in order to enhance the ability to in achieving biaxial texturing in the gold buffer layer 14.

The gold buffer layer 12 utilized in the present invention may be deposited onto the metal substrate 16 by electrodeposition in a chemical bath. Conventional electrodeposition is generally performed at between about 1 and 5 A/cm^2, for between about 1 and 10 minutes. However, as previously noted and shown in Figure 2, conventional electrodeposition of gold does not result in biaxial texturing.

In contrast, the electrodeposition process of the present invention utilizes lower current densities applied over longer time periods when compared to traditional electrodeposition to achieve biaxial texturing in the gold buffer layer 14. In one embodiment, a Ni cathode may be electroplated at a generally constant current density between about 0.10 and 3.5 mA/cm^2 for between about 1 and 60 minutes using a gold plating solution and a Pt anode. In a single deposition under these conditions, the resulting biaxially textured gold layer 12 may have a thickness between about 0.01 and 5 microns.

Thicker films may be produced with increased deposition time and/or a multilayer deposition process in accordance with the present invention. The resulting electroplated gold film 12 has biaxial texturing, which provides an optimal surface for depositing a superconductor material 12 thereon. As used herein, the term "biaxial texturing" refers to both partial and complete biaxial texturing of the gold layer 12, as indicated by X-ray diffraction scans. In embodiments in which the metal substrate 16 is biaxially textured, the electrodeposited gold layer 14 may be epitaxially textured relative to the metal substrate 16 such that the gold layer 14 has the same biaxial crystalline orientation as the metal substrate 16.

After electrodeposition, the biaxial texturing in the gold layer 12 may be increased or enhanced by annealing in a suitable forming gas, such as a gas including hydrogen, argon, nitrogen or combinations. In one example embodiment, the forming gas is a mixture of 4 percent hydrogen in argon. In another example embodiment, the forming gas is a mixture of 10 percent hydrogen in nitrogen. Of course, percentages of hydrogen in nitrogen, argon, or other inert gases can also be used. The annealing process may be performed at between about 500 and 600 °C for between about 12 and 48 hours.

The biaxially textured articles 10 produced according to the present invention may be used in a variety of applications, such as in superconductors, semiconductors, ferroelectrics, pyroelectrics, magnetics, optics, sensors, and semiconductor films. The present invention may be particularly suitable for use with high temperature superconductors, including $Y\text{-}Ba_2\text{-}Cu_3\text{-}O_X$ (YBCO), Bi-Sr-Ca-Cu-O (BSCCO), Tl-Ba-Ca-Cu-O (TBCCO), Pb-Ba-Sr-Ca-Cu-O (PBSCCO), Tl-Sr-Ba-Ca-Cu-O (TSBCCO), Tl-Pb-Sr-Ba-Ca-Cu-O (TPSBCCO), Hg-Ba-Ca-Cu-O (HBCCO). Such high temperature superconducting materials 12 may be deposited on the gold buffer layer 14 by a variety of known methods, including electrodeposition, vacuum deposition, plasma deposition and pulsed-laser deposition, such that the biaxial texturing present in the gold layer 14 is maintained in the superconductor material 12 after deposition. The superconducting

material 12 may be deposited epitaxially, such that the superconducting material 12 has the same crystalline orientation as the gold buffer layer 14.

In a specific example embodiment, YBCO superconductor material 12 may be deposited by pulsed-laser deposition onto a gold buffer layer 14 having biaxial texturing. The biaxial texturing in the gold layer 14 is maintained in the crystalline orientation of the YBCO material 12, so that the superconductor material 12 also has biaxial texturing. The resulting article 10 has a high critical current density optimal for a variety of commercial applications, such as for conductive tapes, current leads, transmission lines, motor and magnetic windings.

The present invention is further characterized by the following examples:

Example 1

Gold was electrodeposited using a commercial gold plating solution including 19 g of Aurovel UP 24 Gold salt manufactured by Lea Ronal, Freeport, NY, which was dissolved in 200 ml deionized water. 800 ml of Aurovel UP 24 makeup liquid concentrate was then added to prepare 1000 ml of plating solution. The solution was then placed in a deposition bath and heated to a temperature of about 65 °C. A gold layer was then electroplated onto a nickel substrate at a current density of 3.3 mA/cm^2 for one minute. Figure 3, a theta-2-theta scan of Example 1, shows c-axis texturing as indicated by the presence of the Au (200) reflection. The presence of the Au (111) reflection indicates that only partial biaxial texturing was formed.

Example 2

The gold layer of Example 1 was annealed in forming gas at 550 °C for 36 hours. Figure 4, a theta-2-theta scan of this annealed electrodeposited gold layer, shows increased or improved c-axis texturing in the gold layer, as indicated by the increased intensity of the Au (200) reflection as compared to Figure 3. The presence of the Au (111) reflection indicates that only partial biaxial texturing was formed.

Example 3

Gold was electroplated according to Example 1 except that the gold layer was electrodeposited at a current density of 0.13 mA/cm^2 for 45 minutes. Figure 5, a theta-2-theta scan of Example 3, shows the presence of c-axis texturing as indicated by the presence of the Au (200) reflection. The presence of the Au (111) reflection indicates that only partial biaxial texturing was formed. Additionally, Figure 6, a pole scan of the electrodeposited gold layer, shows the presence of partial biaxial texturing.

Example 4

The gold layer of Example 3 was annealed in forming gas at 550 °C for 48 hours. Figure 7, a theta-2-theta scan of this annealed gold layer shows increased c-axis texturing in the gold layer, as indicated by the increased intensity of the Au (200) reflection. The absence of an Au (111) reflection indicates complete biaxially texturing.

Figure 8, a pole scan of the annealed electrodeposited layer of gold (measured at HKL 111 intensity), also indicates complete biaxial texturing of the gold layer. Figure 9 is an omega scan of this annealed electrodeposited gold layer, which shows a full-width-at-half-maximum (FWHM) of only 8°. Figure 10 is a phi scan of this annealed electrodeposited gold layer, which shows a (FWHM) of only 5°. Figures 9 and 10 indicate a very high quality film with a low population of high misorientation angles.

Example 5

Gold was electroplated according to Example 1, except that the gold layer was electrodeposited at a current density of 0.3 mA/cm^2 for 35 minutes. Figure 11, a theta-2-theta scan of the electrodeposited gold layer, shows the presence of c-axis texturing as indicated by the presence of the Au (200) reflection. The presence of the Au (111) reflection indicates that only partial biaxial texturing was formed.

Example 6

The gold layer of Example 5 was annealed in forming gas at 550 °C for 12 hours. Figure 12, a theta-2-theta scan of this annealed electrodeposited gold film, shows complete c-axis texturing of the gold film as indicated by the increased intensity of the Au (200)

reflection and the absence of an Au (111) reflection. Figure 13 is a pole figure scan of this annealed electrodeposited gold layer (measured at HKL 111 peak), which also demonstrates complete biaxial texturing of the gold layer.

Example 7

Gold was electroplated according to Example 1 except that the gold layer was electrodeposited at a current density of 0.13 mA/cm^2 for one hour. The gold layer was then annealed in forming gas at 550 °C for 48 hours. Figure 14, a theta-2-theta scan of this electrodeposited gold layer after annealing, indicates complete c-axis texturing, as indicated by the presence of the Au (200) reflection and the absence of the Au (111) reflection.

Example 8

YBCO was electroplated by pulsed-laser deposition onto an electrodeposited gold layer produced according to the present invention. Figure 15, a theta-2-theta scan of the resulting article shows the presence of reflections 002, 003, 103 and 105. These reflections indicate that YBCO having biaxial texturing can be grown onto a biaxially textured gold substrate formed according the present invention.

The foregoing description and the illustrative embodiments of the present invention have been presented in detail in varying modes, modifications, and alternate embodiments. It should be understood, however, that the foregoing description of the best modes of the present invention is exemplary only, and that numerous other modifications and alternative embodiments and modes of the invention will readily occur to persons skilled in the art. Therefore, the scope of the present invention is to be limited only by the claims below, as properly interpreted by applicable law, and not by the exact constructions, process steps, or parameters shown or described above.

The words "comprise," "comprises,", "comprising," "include", "including", and "includes" when used in this specification or in the following claims are intended to be open-ended, i.e., to specify the presence of stated features or steps, but they do not

preclude or exclude the presence or addition of one or more features, steps, or groups thereof, which are not stated or recited.